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CASTABLE EXPLOSIVE COMPOSITIONS BASED ON
DINITROPROPYLACRYLATE AND HMX

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By

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DDC

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FOREWORD

The investigation of 2,2-dinitropropylacrylate as a castable, polymerizable binder for explosives was first undertaken at NOTS in 1962. Need for a cast explosive with higher energy potential than that of PBXN-101 and better heat resistance than that of relatively low melting TNT-based compositions led to further development and subsequent improvement of the HMX/DNPA system in 1965-1966. A report published in October 1966 describes the initial stages of this work. Additional studies to increase energy and improve processability have continued during the past year. Results are described in the present report.

This project was conducted under Task Assignment ORD-033-201/200-1/F009-08-05 and was reviewed for technical accuracy by Dr. H. J. Gryting and Dr. C. D. Lind.

Any reference to specific source or brand name does not necessarily imply Government indorsement of any particular product.

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Under authority of
G. W. LEONARD, Head,
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ABSTRACT

The castable explosive, HMX/dinitropropylacrylate, was improved by
formulation modifications to obtain higher energy, better physical
properties and stability, and greater efficiency in preparation. Use of
volatile liquids in mixing operations, special casting techniques, and
selection of optimum HMX particle size blends resulted in solids loadings
of 87% and higher with corresponding detonation velocities exceeding
8600 meters per second. Optimization of monomer inhibitor concentration
made it possible to eliminate pre-processing DNPA purification, yet at
the same time obtain adequate storage stability. Use of a new curative,
cobalt acetyl acetonate, greatly facilitated curing by reducing time
and temperature and eliminating the necessity for oxygen exclusion.
Resulting castings were harder, more uniform, and more stable, with
150°C VTS values as low as 2.4 cc/g/48 hours.

Two new copolymers of DNPA were prepared and evaluated as energetic
binders, one with difluoraminopropylacrylate, the other with dodecafluoro-
heptylacrylate. Detonation velocities, as predicted by computation, were
comparable to those for DNPA homopolymer at equivalent HMX loadings.
(Confidential)

LIST OF ABBREVIATIONS

HMX	cyclotetramethylenetetranitramine
PBX	plastic-bonded explosive
DNPA	2,2-dinitropropylacrylate
NFPA	2,3-bis(difluoramino)propylacrylate
C_5A	1,1,5-trihydrooctafluoropentylacrylate
C_7A	1,1,7-trihydrododecafluoroheptylacrylate
C_9A	1,1,9-trihydrohexadecafluorononylacrylate
CoAA	cobalt acetyl acetonate
tBPB	t-butyl perbenzoate
tBHP	t-butyl hydroperoxide
DTA	differential thermal analysis
TGA	thermal gravimetric analysis
VTS	vacuum thermal stability
PBXN-101	HMX/polyester-styrene 82/18
BDNPF-BDNPA	bis-2,2-dinitropropyl formal-bis-2,2-dinitropropyl [acetal
FEFO	bis-(2,2-dinitro-2-fluoroethyl)formal
HQ	hydroquinone
MEHQ	hydroquinone methyl ether (p-methoxyphenol)
NDPA	nitrodiphenylamine
ptBC	paratertiary butyl catechol

ACKNOWLEDGEMENTS

CONTENTS

CASTABLE EXPLOSIVE COMPOSITIONS BASED ON
DINITROPROPYL ACRYLATE AND HMX

INTRODUCTION

Background

In the latter part of 1965 a program was undertaken at NOTS to
develop an improved castable plastic-bonded explosive. This product,
to be of value in advanced weapons applications, was to have energetic
potential approximating that of PBX 9404[1] or of some of the best TNT-
based formulations such as octol.[2] However, unlike the latter, the new
composition should be able to withstand temperatures up to 150°C with
no significant physical or chemical changes. Other desirable character-
istics would include safety in formulating and handling, ease and
convenience in processing, and ready availability and low cost of in-
gredients. Resistance to vibration and thermal shock might also be
critical.

Initial survey of possible candidate components indicated that HMX
combined with the energetic monomer, 2,2-dinitropropyl acrylate might
be a promising choice. Studies carried out to verify the feasibility
included investigations of stability, energetic potential, and process-
ability. A report has been published which describes the results of
this work (Ref. 2).

Preliminary findings indicated that HMX-dinitropropyl acrylate
compositions might be capable of fulfilling many of the desired
objectives. The low viscosity of DNPA monomer permitted HMX loadings
of 85%, which, together with the inherent energy of the binder material
itself, resulted in detonation velocities higher than 8500 meters per
second. In addition, the heat resistance of these compositions
appeared to be good, with autoignition points averaging 225°C, and 150°
vacuum thermal stability values ranging from 3 to 6 cc for a forty-
eight hour period. The DNPA itself, although an energetic material,
was insensitive to initiation by impact or friction and it acted as a
desensitizing agent for HMX, raising the impact value to approximately
that of tetryl.

Physical properties of cured DNPA binder, with and without filler,
appeared advantageous. With proper selection of curing agents and
curing conditions the polymerized product was a tough, resilient solid

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[1] Compressible PBX developed at Los Alamos, 94% HMX, 3% tris(β-
chloroethyl)phosphate, 3% nitrocellulose; detonation velocity 8710 m/sec
at 1.821 g/cm^3 (1/2-in. diameter). (Ref. 1.)

[2] 75% HMX/25% TNT, detonation velocity 8643 m/sec at 1.81 g/cm^3.

with little or no visible change occurring after brief exposure to 150°C temperatures. The monomer appeared to copolymerize readily with other unsaturated compounds, including polyesters, fluoroacrylates and nitro derivatives such as petrinacrylate. Furthermore, a survey of possible sources for DNPA revealed at least three manufacturers capable of supplying the material in laboratory quantities and interested in meeting eventual production demands. All suppliers anticipated that costs would decrease substantially with increased production and experience.

While initial studies were encouraging, they also pointed out some shortcomings or areas requiring further improvement. One of these was processability. Curing, for example, was lengthy and exacting, and required at least 80°C temperatures and exclusion of atmospheric oxygen. Moreover, physical consistency of cured polymer varied somewhat from batch to batch. Mixing in the initial stages could be hazardous before the HMX was thoroughly wetted by the binder. Also energy fell somewhat short of the desired goal. Although detonation velocity measurements showed a significant advantage over PBXN-101 or Composition B,[3] values were still inferior to those for octol or PBX 9404.

Since publication of the first report additional experimental work has effected a solution for many of these problems and has afforded better insight into others. It is the purpose of the present report to bring up to date the available information concerning the development of the HMX/DNPA system. Significant progress has been made in respect to energy improvement, greater ease and safety in processing, better physical characteristics and stability, and increased knowledge concerning availability and variability of basic constituents. Several interesting new DNPA copolymers have been prepared including one based on a difluoramino derivative. Additional Ruby calculations have been carried out to predict the performance of such binder systems. Results of these computations, it is found, correlate well with actual test data.

Present Status

ENERGY. With improved solids loading and processing techniques it has been possible to raise the detonation velocity of HMX/DNPA compositions to more than 8600 m/sec. By combining accumulated small contributing factors it may be possible to gain still another 100 m/sec. Beyond 8700, further advances are expected to become increasingly difficult with this particular system.

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[3] 8000 m/sec average. See Ref. 3.

PROCESSABILITY. Use of a new curing accelerator, cobalt acetyl acetonate, has eliminated most of the previous curing difficulties and has reduced curing requirements. Cures which formerly necessitated 80°C temperatures for several days with oxygen rigidly excluded now can be successfully accomplished at 50-60°C overnight in air. The resulting product is not only harder and more solid than previously, it is also more resistant to thermal decomposition as evidenced by vacuum thermal stability tests. Furthermore, the process is more tolerant of contaminants such as residual traces of inhibitor. Some samples of monomer which consistently failed to cure adequately in earlier work can now be polymerized to yield excellent castings.

SAFETY. Two processing modifications to achieve higher solids loading under safer operating conditions offer considerable promise. One involves the use of volatile desensitizing liquids during preliminary stages of mixing. Inexpensive, non-flammable compounds such as dichloromethane added to HMX and DNPA components prior to mechanical mixing provided sufficient fluidity to permit solids loadings higher than 87% with no sacrifice in the quality of the final casting. The liquid was readily removed by evaporation during latter stages of mixing. Subsequent castability and curability were excellent, and the final cured material was dense, solid, and visibly void-free with detonation velocities exceeding 8600 meters per second.

A second approach involving more technical difficulties but possibly offering still greater advantages in respect to safety and loadability utilizes a prepacked bed of HMX infiltrated by the low viscosity liquid binder and then cured under pressure. Additional work is needed to fully investigate and substantiate the feasibility of employing the latter technique.

AVAILABILITY. DNPA monomer obtained from three different manufacturers was found to be consistent in respect to processability and properties. Products from all three sources were compounded with HMX to yeild compositions of comparable sensitivity, thermal stability and physical consistency.

STABILITY. A number of different additives in DNPA/HMX formulations failed to improve thermal stability when evaluated by means of DTA, TGA and 150°VTS. However, as pointed out previously, use of cobalt acetyl acetonate as a curative, besides greatly facilitating polymerization, also improved vacuum thermal stability and weight loss at elevated temperatures. Prior to the use of CoAA, some of the volatile matter evolved during VTS tests was identified as free monomer. More effective polymerization methods reduced the amount of this product.

Surveillance of DNPA monomer showed outstanding stability to both polymerization and degradation. Several months of storage at 50°C, for example, failed to produce detectable polymerization, even in the case

of essentially inhibitor-free monomer. Thus, it may be possible in production applications where material is utilized rather rapidly to substantially reduce or even eliminate the use of inhibitors such as hydroquinone, which presently are being removed by tedious and lengthy washing processes before the monomer is cured.

CURING OF DINITROPROPYLACRYLATE COMPOSITIONS

Dinitropropylacrylate monomer used in compounding HMX/DNPA explosive compositions was obtained from three suppliers, Aerojet General Corporation, Hummel Chemical Company, and Northrup-Carolina (Appendix A). A total of six different shipments was evaluated. All were essentially equivalent except for inhibitor content. With proper selection of processing conditions all produced castings of acceptable strength and comparable stability. A brief description of the six monomer lots and their behavior is given in Table 1. Vacuum thermal stability curves after compounding and curing are shown in Fig. 1.

Early Problems

Initial work described in earlier reports was carried out solely with Aerojet material. Difficulty in obtaining consistent and complete curing led to a study of various initiator systems including mixed or synergistic peroxides (Ref. 2). Best results were achieved under the following conditions:
    Binder - 95% 2,2-dinitropropylacrylate, 5% acetyltriallyl citrate[4]
    Accelerator - 0.1% dimethylaniline
    Curatives - 0.5% each t-butyl perbenzoate and t-butyl hydroperoxide
    Temperatures - 60°C overnight followed by 80°C 24-48 hours
    Atmosphere - nitrogen
The resulting polymer was amber in color, resilient, tough and relatively free from tack provided adequate precautions were taken initially to remove inhibitor either by distillation or by washing with dilute caustic. Attempts to reduce curing time or temperature or to cure in air resulted in incomplete polymerization with very inferior physical properties.

When a new shipment of monomer was obtained from a different supplier, namely, Hummer DNPA inhibited with 0.1% p-methoxyphenol, use of the described curing procedure resulted in total failure. Extensive purification techniques were tried in an effort to remove the inhibitor sufficiently to obtain gelation. These included double distillation at reduced pressure, multiple washes with caustic, extraction with MgO, and various combined procedures (described in Appendix B). In addition, several different curing systems were tried including omission of dimethylaniline and substitution of methyl-n-amyl-ketone peroxide for the tBPB-tBHP system. All failed to cure Hummel material satisfactorily and in most cases it was not even possible to obtain gelation.

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[4] Crosslinking additive to prevent plastic deformation at elevated temperatures.

TABLE 1. Properties and Processability of DNPA From Various Sources

Source	Lot	Appearance	Approx viscosity, centistokes[a]	Index of refr[b]	Curing requirements	Cured properties with HMX filler		
						Appearance	Autoign pt, °C	VTS, 150°C ml/g/48 hr
Aerojet	Rec'd 7-11-62 Methylene blue inhibitor	Inky blue as rec'd, yellow-green after distillation	5-6	1.46	Must be distilled. Cures readily 60-80°C with several initiators	Tough, solid, resilient, fairly hard	222	3.4
Aerojet	Rec'd 12-21-65 AGC 4651-2 0.02% HQ	Pale yellow before and after purification	5-6	1.46	Not critical, must be distilled or NaOH washed	Tough, solid, slightly flexible, fairly hard	220	4.2
Aerojet	Rec'd 1-13-67 AGC 06824 0.02% HQ	Golden yellow, lighter after washing	5-6	---	Very satisfactory if NaOH washed	Tough, hard, solid, resilient	225	2.8
Hummel	Rec'd 4-66 NL-12-36 0.1% MEHQ	Light golden yellow, sl darker than Aerojet	5-6	1.46	Requires NaOH washing and CoAA initiator. No cure without CoAA	More flexible and softer than above but solid and strong	221	3.2
Hummel	Rec'd 8-66 NL-12-73-6-228, no added inhibitor	Pale yellow, sl darker than washed Aerojet	Not detd similar to above	1.46	No purification reqd if CoAA used	Hard and tough, solid and strong	221	3.3
Northrup-Carolina	Rec'd 9-66 8996-42 0.005% MEHQ	Yellow-amber darker than previous sources	5-6	---	Not critical if washed and CoAA employed	Strong, flexible, sl surface porosity	225	3.5

[a]Determined by micro method (Ref. 2) at 24°C.

[b]24°C.
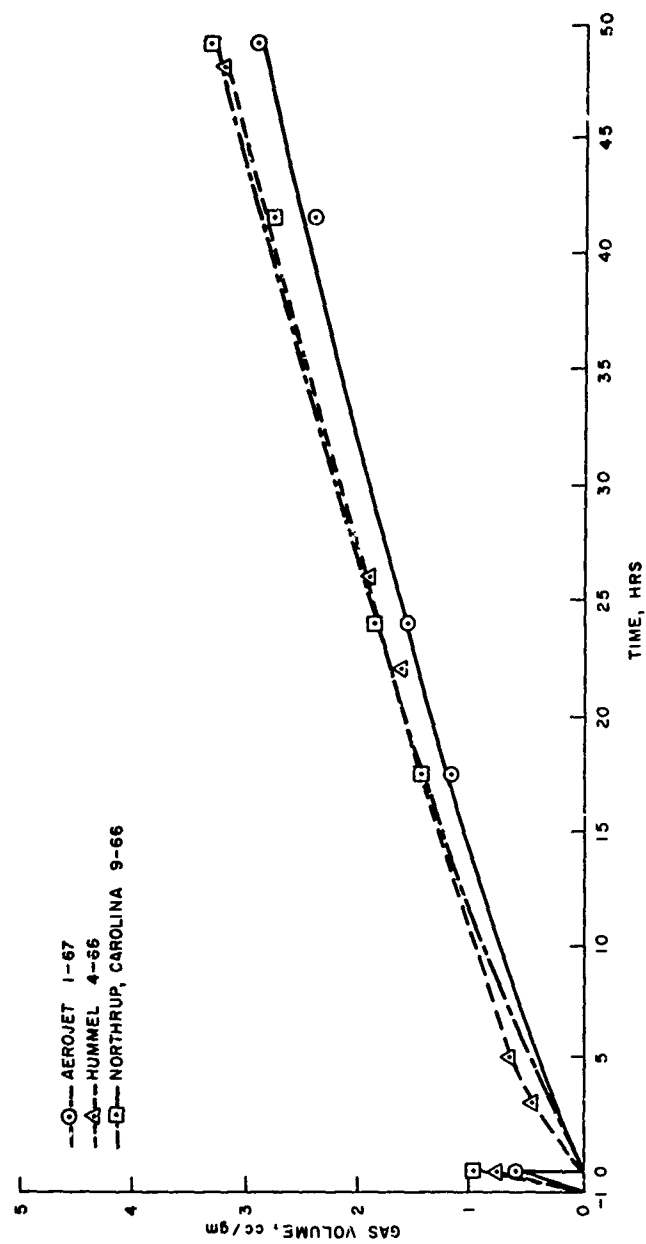
FIG. 1. 150°C Vacuum Thermal Stability of HMX/DNPA Compositions Containing DNPA From Various Sources. 20% Binder with 5% ATAC Crosslinker. CoAA Cure at 60°C. Reevacuated After One Hour.

The best procedure was a triple extraction with caustic. Monomer thus treated gelled; however, was very weak and tacky. With HMX filler cohesion and strength were unacceptable. Aerojet DNPA treated by the same methods continued to cure adequately provided the specific conditions of time, temperature and ambient atmosphere prevailed. Since infrared studies and other observations indicated no significant differences between the two monomer lots, it was concluded the variation in polymerization behavior must be due to trace impurities or residual inhibitor not readily removable or detectable.

Two methods of approach were used to solve the problem: (1) establish minimum inhibitor levels and types of inhibitor necessary for adequate storage stability, (2) search for a better catalyst system. Both approaches proved successful. Hummel DNPA with no inhibitor added after synthesis cured satisfactorily, yet showed no evidence of deterioration after three months of storage at 50°C. In addition, a very effective curing agent was found: cobalt acetylacetonate.

COBALT ACETYLACETONATE. Cobalt II is frequently used in conjunction with peroxide curatives to initiate vinyl polymerization. The usual compound, the naphthenate salt, which served effectively to promote curing in earlier cast PBX compositions, could not be used with DNPA because of its insolubility. More recently a greater variety of heavy metal and transition metal derivatives have become available for use in other polymerization applications. Among these newer introductions are cobaltous propionate, octoate, and acetylacetonate. It was felt that one of these might have solubility characteristics such that cobalt II could be successfully introduced into DNPA binder compositions.

The propionate appeared to be essentially insoluble in DNPA, while the octoate only dissolved to a slight extent. The acetylacetonate, however, when finely ground and well dispersed, could be readily dissolved at concentrations somewhat higher than 0.2 percent.

Cures resulting from the use of CoAA were most encouraging. Its effectiveness when compared with other accelerators under minimum curing conditions is shown in Table 2. Among the advantages were lower curing temperatures, shorter curing times, and tolerance of oxygen during cure. Furthermore, acceptable cures were obtainable with all sources of DNPA, including MEHQ inhibited Hummel washed only once with caustic. Physical properties without and with HMX filler were very promising and the filled compositions were hard, solid, and tough with no evidence of instability or incompatibility due to the new additive. Vacuum thermal stability appeared to improve with CoAA inclusion. Measurements representing a number of different samples and DNPA sources are plotted in Fig. 2. Without CoAA, greater volatility and weight loss were observed. Also more liquid condensate was noted in the VTS tubes. This product was indicated by IR to be free DNPA monomer. By effecting more complete polymerization, therefore, CoAA may thus improve high temperature stability as well as physical properties and processability.

TABLE 2. The Effect of Various Accelerators in Curing DNPA

Accelerator	DNPA source	Curing conditions[a]			Cured appearance
		Temperature, °C	Time	Atmosphere	
None	Aerojet, distilled or washed	60→30	48 hr	N_2	Tough, flexible, solid Tacky, incompletely cured
	Hummel, 0.1% MEHQ,distilled or washed	with less time, temp or in air			
		80	2-3 days	N_2	Failed to cure
Dimethyl aniline 0.1%	Aerojet, distilled or washed	60→80	48 hr	N_2	Tough, hard, solid, resilient
	Hummel, 0.1% MEHQ,distilled or washed	with less time, temp or in air			Failed to cure
		80	2-3 days	N_2	Failed to cure
Cobalt acetyl Acetonate	Aerojet, washed	50	18 hr	air	
		60	18 hr	air	Hard & strong, well cured
0.1 - 0.2%	Hummel, 0.1% MEHQ,washed	60→80	48 hr	N_2	
	Hummel, uninhibited	60	18 hr	air	
	Northrup, washed	60	18 hr	air	
Cobalt naphthenate	Aerojet, distilled	---	---	---	Insoluble in DNPA, forms scum
Cobalt propionate	Aerojet, washed	---	---	---	Insoluble in DNPA
Cobalt octoate	Aerojet, washed	60→80	48 hr	N_2	0.1% failed to dissolve completely otherwise properties good

[a] tBPB and tBHP initiators used, 0.5% each.
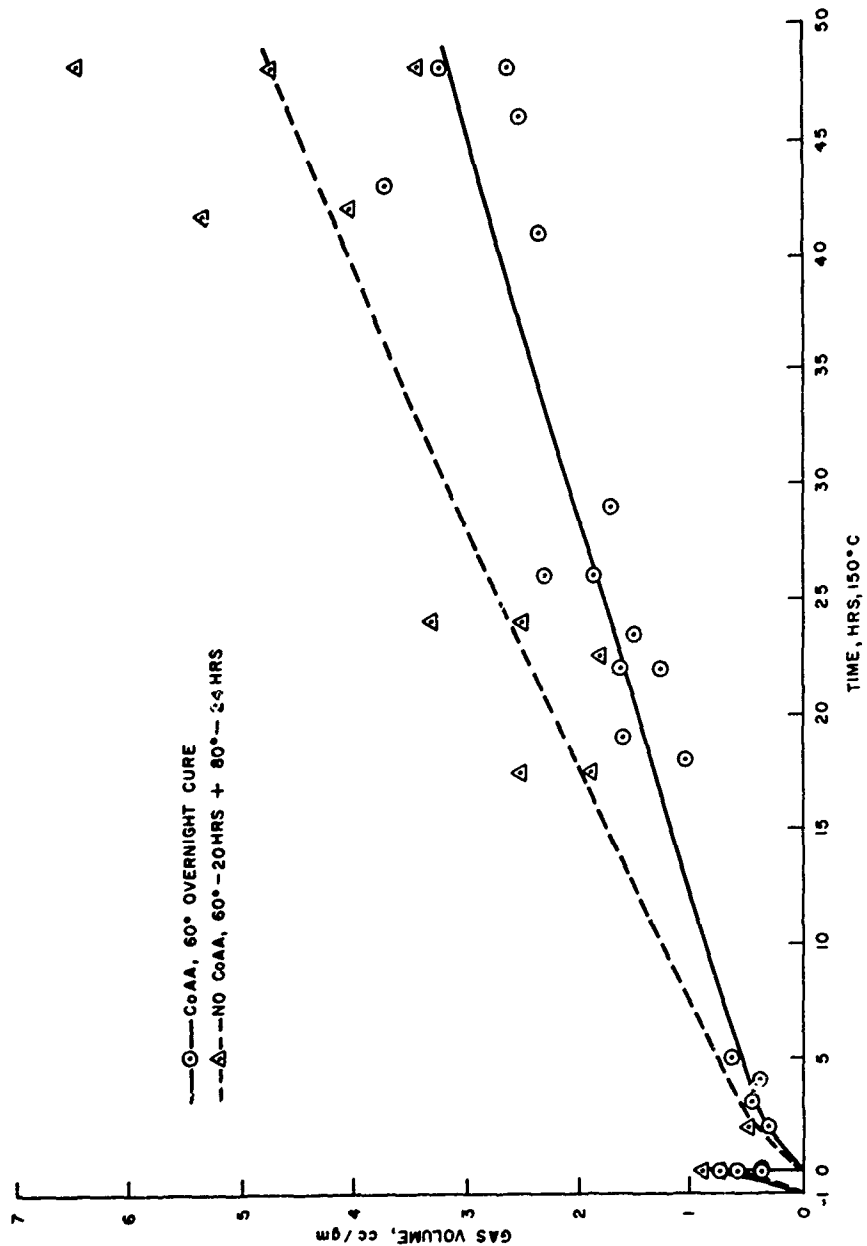
FIG. 2. Vacuum Thermal Stability Curves for HMX/DNPA with and without CoAA.

To further evaluate the efficiency of CoAA accelerator, tests were performed to determine the minimum temperature at which DNPA binder containing 0.1% CoAA and 0.5% each tBPB and tBHP could be cured. Results indicated that overnight cures at 50°C were essentially as good as those at 60°C. At 40°C the resulting polymer was qualitatively weaker and softer but nevertheless well gelled and rigid. At ambient temperature gelation occurred within several days, but acceptable strength and hardness were not achieved within a reasonable length of time. These samples, however, could be further cured at 60°C to obtain the usual strength, rigidity and freedom from tack. Such step-curing techniques, gelation at ambient followed by post curing at a higher temperature, may prove advantageous in applications where polymerization exotherms might constitute a processing hazard; for example, in larger warheads where heat cannot be readily dissipated.

The effect of low temperature curing on thermal stability is shown in Fig. 3 where VTS curves are plotted for samples cured at room temperature only, and at 40 and 50°C. The compositions were stored for approximately one month under ambient conditions prior to testing.

MONOMER INHIBITION. Experience with the two Hummel samples indicated the advisability of maintaining inhibitor levels at as low a value as permissible, both to simplify purification procedures and produce better castings. Therefore, accelerated aging tests were conducted to determine the minimum concentration and the most efficient type of inhibitor to protect against premature polymerization in storage. Eleven monomer samples were stored in an oven at 50°C. These included three batches of inhibited DNPA as received from the various suppliers as well as a special shipment from Hummel to which no inhibitor had been added after esterification. Additional samples were prepared by adding known amounts of ptBC, hydroquinone, and MEHQ to the "uninhibited"[5] Hummel material. Approximately 3-ml monomer samples were placed in glass tubes 12.8 cm by 5 mm ID with about 1/4-inch of air space above each liquid surface. Each tube was then stoppered, placed in the oven, and periodically observed for possible polymerization by cooling to 25°C, inverting, and measuring the rate of time for the air bubble to rise.

At the end of 90 days the bubble viscosity test failed to reveal any significant change or difference in any of the samples. The test was then discontinued and the samples were further evaluated by IR, DTA, and observing ability to polymerize after extraction of the inhibitor. Results of these tests are summarized in Table 3. Both IR and DTA failed to reveal differences between samples or degradation when compared with

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[5] Suitable test procedures are being sought to analyze this material for residual traces of inhibitor. The manufacturer estimates concentrations to be negligible.
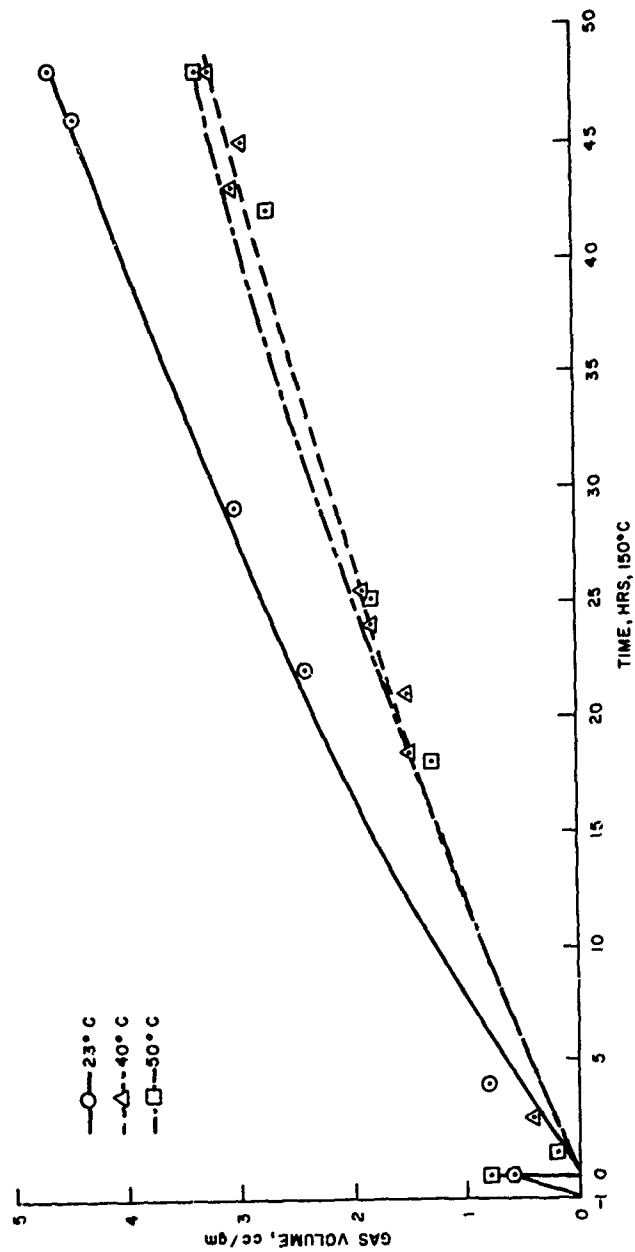
FIG. 3. The Effect of Curing Temperature on the Vacuum Thermal Stability of HMX/DNPA, 20% Binder containing 5% ATAC, 0.1% CoAA, 0.5% each tBPB and tBHP. (Hummel uninhibited DNPA.)

TABLE 3. The Effect of 90 Day, 50°C Storage on DNPA Monomer

DNPA Source	Nominal Inhibitor Content	Change in Viscosity Bubble Rise, sec.		DTA, °C Ignition[a] Exotherm	Peak	Polymerizability[b]
Aerojet, as rec'd	0.02% HQ	2.3	↑	201	224	Flexible, solid, tack free strong.
Hummel, as rec'd	0.1% MEHQ	2.2	↑	205	224	Tackiest and most flexible of group. Relatively dark in color.
Hummel, un-inhibited	Residual only from esterification step	2.2	↑	196	224	Firm, no tack, quite flexible.
Northrup-Carolina	0.005% MEHQ	2.3	↑	191	224	Relatively flexible but not tacky.
Hummel, un-inhibited	Residual +0.001% HQ	2.2	↑	189	224	Similar to uninhibited Hummel entry No. 3.
Hummel, un-inhibited	Residual + 0.01% HQ	2.5	↑	179	226	Moderately hard, less flexible than uninhibited Hummel.
Hummel, un-inhibited	Residual +0.02% HQ	2.5	↑	201	224	Harder and less flexible than uninhibited Hummel, darker.
Hummel, un-inhibited	Residual +0.001% ptBC	2.5	↑	205	222	Similar to uninhibited Hummel.
Hummel, un-inhibited	Residual +0.01% ptBC	2.6	↑	202	224	Similar to uninhibited Hummel.
Hummel, un-inhibited	Residual +0.001% MEHQ	2.5	↑	204	222	Similar to uninhibited Hummel.
Hummel, un-inhibited	Residual +0.01% MEHQ	2.7	↑	203	224	Harder and less flexible than uninhibited Hummel.

a Onset point. Somewhat difficult to assess due to volatilization of sample.
b Samples were washed with caustic and cured with 5% ATAC, 0.1% CoAA, and 0.5% each tBPB and tBHP.

NOTE: There was no change in IR analysis on any of the samples tested. Standards for evaluation were unexposed monomer and poly-DNPA prepared both at NOTS and Aerojet.

unexposed controls. Polymerization tests showed slightly increased curing
rates as a result of aging the monomer. This effect can probably be
attributed to partial decomposition of the inhibitor resulting in lower
concentrations which are less difficult to remove.

Both the CoAA and the surveillance studies point to a conclusion
which is very significant in respect to efficiency in compounding DNPA
based formulations. By using optimum inhibitor types and concentrations
it is possible to supply monomer which will undergo severe storage
conditions, yet will polymerize readily to give an excellent end product.
Moreover, this polymerization may be effected with no lengthy distillation
or washing procedures requiring considerable labor and extensive equipment.

ATTEMPTS TO INCREASE ENERGY THROUGH HIGHER SOLIDS LOADING

Experimental evidence obtained from measurements with HMX/DNPA
formulations indicates that increases in detonation velocity of more than
100 meters per second may be realized with each additional 2% of HMX at
80-90% solids loading (Fig. 4). While this source of energy per se may
be fairly limited, nevertheless when coupled with other contributing
factors such as binder modification or inclusion of dense or oxidizing
constituents, the additive effect may be sufficient to produce substantial
gains. Therefore, attempts have continued to obtain the maximum HMX
loading consistent with processability.

Studies completed at an earlier date (Ref. 2) showed that with a low
viscosity binder such as DNPA, solids loadings of 85% were entirely feasible.
Further work with inert simulant binders indicated that 2-3% higher loadings
might be possible and processable provided HMX particle size distribution
was optimized and carefully controlled. These studies were all carried
out with conventional mixing and casting equipment.

A serious disadvantage in formulating highly filled, castable mixes
of the type in question results from the sensitivity of the HMX before
it is wet by the binder. Precoating the explosive with a desensitizing
agent has been used in some explosive applications to overcome this
difficulty (Ref. 3). However, at the binder levels involved in the
present work (i.e., 12%) replacing part of the monomer with an inert
desensitizing agent will sacrifice the energy advantages gained by the
higher filler level.

Prepacked Bed Method

One possible approach to obtain higher loading unaccompanied by
extreme mixing hazards is to combine ingredients after the filler has
been introduced and dried in the mold. This method was investigated at
NOTS in 1959 by H. Stanton (Ref. 4) in a series of preparations in which
HMX prepacked into molds was vacuum dried and then wet by monomers
introduced by suction. The work was not continued beyond the laboratory

stage because of design difficulties in adapting to actual weapons and
to a greater extent because development of the PBXN-101 castable system
satisfied existing needs more readily and more economically.

High solids loading with TNT-based compositions in prepacked molds
has been obtained by a German process (Refs. 5,6). This method employs
a perforated disk which is rammed into the top of the filled mold cavity.
Excess molten TNT, the constituent of lower energy, is forced upward
through the perforations and is separated and removed from the main
charge.

For HMX/DNPA, a procedure was tried which includes variations of
both the Stanton and German procedure. A sketch of the equipment used is
shown in Fig. 5.[6] Solids loadings of over 90% were obtained. However,
experimental difficulties and failure to obtain homogeneous castings
indicate the necessity for considerably more study before the procedure
can be adapted to production needs.

Basically, the process involves loading the mold from the top with
wet HMX of optimum size distribution for maximum packing. Suction is
then applied from the bottom by means of an aspirator to pack the bed and
dry the HMX. A filter pad and reinforcing screen prevent the explosive
from being pulled through. The aspirator is then disconnected and re-
placed by a delivery tube leading from a container of binder. Vacuum is
applied at the top of the mold until the liquid binder appears in the
riser tube. As at the bottom, a filter pad and perforated plate retain
the HMX. Binder supply and vacuum source are then disconnected and the
mold assembly is next placed in a jig. Pressure applied in the longitudinal
axis by means of a screw forces excess binder from the top and bottom
orifices by depressing the piston-shaped top plug. The composition is
then cured in the jig without relieving pressure.

The procedure described is attractive for the following reasons:

1. Theoretically loadability should be limited only by packing
factors.
2. The method involves no actual handling of dry HMX. Explosive
can be introduced into the mold either wet with water, or to facilitate
drying, rinsed with a more volatile liquid such as methanol.
3. Hazards due to mechanical mixing are eliminated.
4. Air may be readily excluded during cure if oxygen inhibition is
a problem.

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[6] The assistance of R. Eppinger and J. Eldridge is acknowledged in
suggesting improvements for the technique outlined.
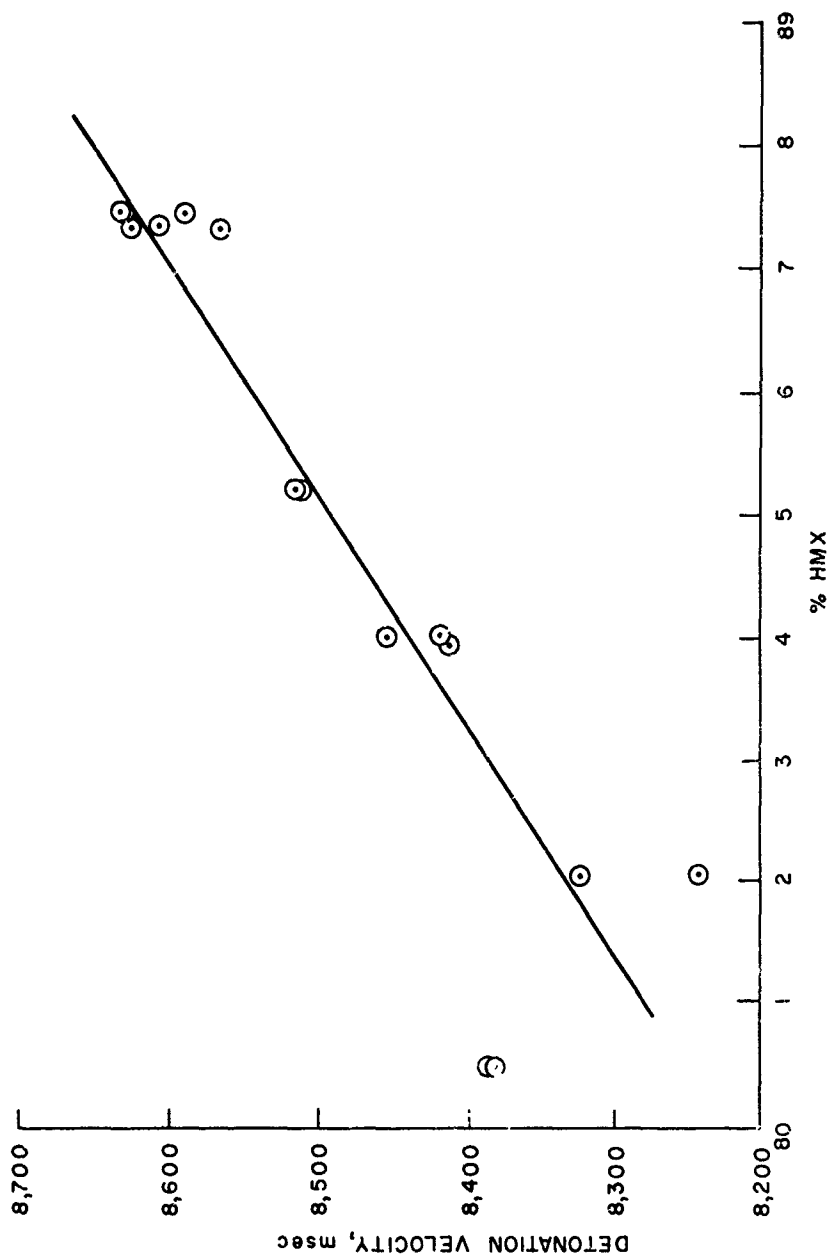
FIG. 4. The Effect of HMX Loading on Detonation Velocity; HMX/DNPA Compositions.
NOTE: Each point represents one test shot.

VACUUM SUPPLY

CYLINDRICAL TEFLON PISTON

BINDER SUPPLY

MOLD

MOLD CAVITY

REINFORCING SCREENS

FILTERS

ASPIRATOR

I PACKING AND FILLING

SCREW

BOTTOM PLUG

TOP PLUG (TEFLON CYLINDER)

LOADED MOLD

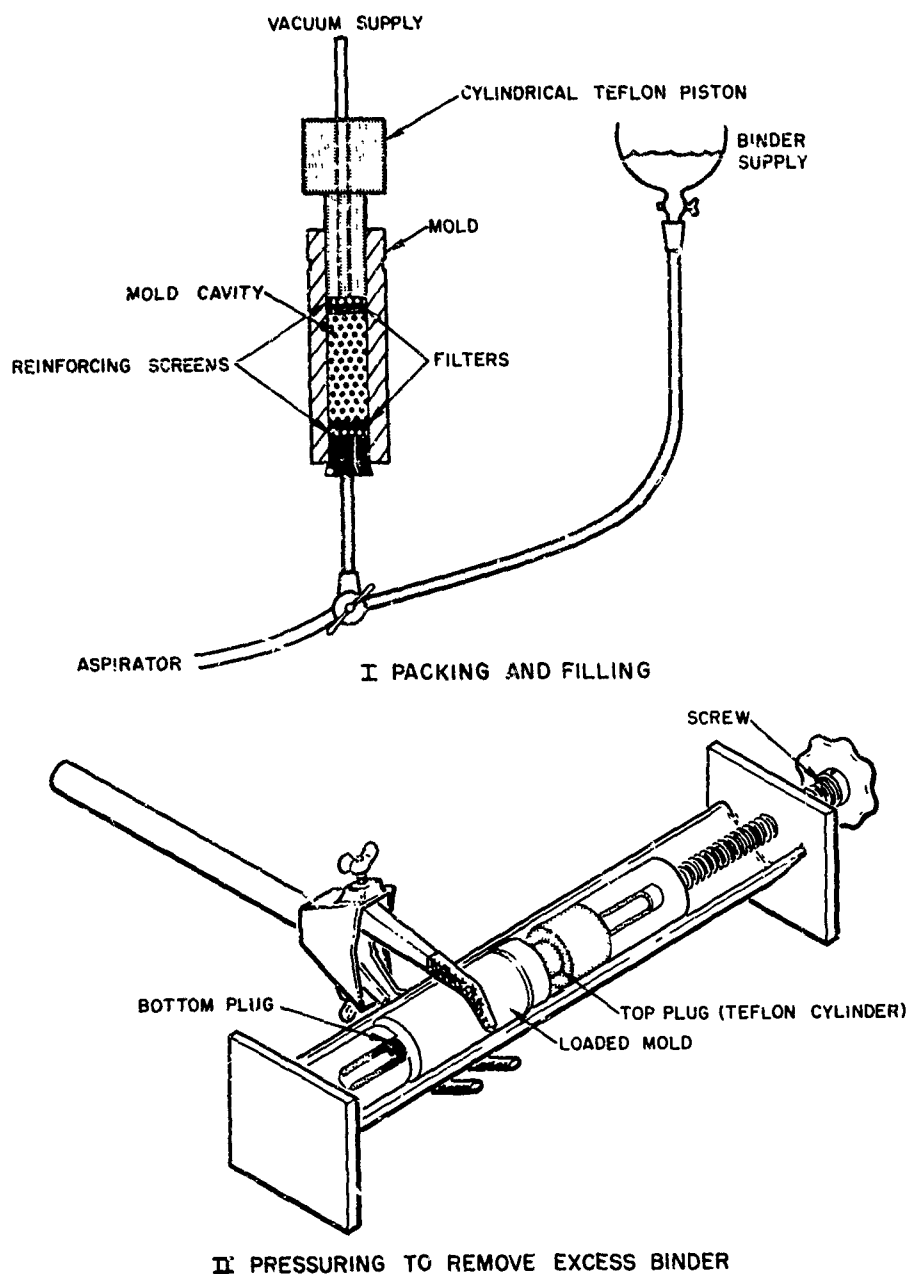II PRESSURING TO REMOVE EXCESS BINDER

FIG. 5. Equipment Used for Prepacked Bed Method of Loading.

However, actual practice was not as straightforward as theory would seem to indicate. Removal of the desensitizing liquid (water or methanol) was difficult and time consuming. When HMX mixtures of optimum packing density were used, not only was drying prolonged, but also subsequent penetration of the bed by the binder was made very difficult. Use of excessive vacuum resulted in loss of volatile components such as styrene in Laminac binders, so that the residual resin failed to cure adequately. Even with low viscosity non-volatile monomers such as DNPA, bed penetration was so time consuming that a compromise was necessary in selecting HMX blends. This, in turn, resulted in inferior packing and lower solids loading.

A brief summary of the compositions prepared by the prepacked bed loading procedure is shown in Table 4. Included are observations concerning flow rates for both actual and simulant binders through beds of varying density. It is obvious that improvement is needed both to increase efficiency and produce castings of better homogeneity. However, the eventual advantages of the described system if successful should warrant the expenditure of additional effort to insure that no reasonable possibility has been overlooked.

Desensitization During Mixing

Another approach to achieve high solids loading with reduced processing hazard was based on addition of a volatile fluid desensitizer prior to mixing. This nonreactive liquid could then be removed readily by evaporation after the relatively non-volatile DNPA binder was dispersed sufficiently to wet and desensitize the HMX filler. While not offering the promise of as high ultimate loadability perhaps as the prepacked bed method, the latter, however, appeared to be more readily adaptable for immediate use with existing equipment on both a small and large scale.

A liquid, to be suitable for the intended application, should have the following characteristics: It should thoroughly wet the HMX and provide adequate interparticle lubrication and cushioning to minimize internal friction during the mixing process. It should have no solvent effect on HMX to alter particle size. It should be compatible and non-reactive with every component in the formulation. Preferably, it should be non-flammable and have high heat capacity, and lastly, it should be cheap and readily available. The latter two characteristics are of secondary importance since recovery and reuse could be readily accomplished.

For initial evaluation a number of liquids were examined in the laboratory by mixing with weighed quantities of HMX and subsequently adding DNPA binder. Vacuum and heat were then applied to remove the volatile liquid. When evaporation appeared to be essentially complete, time and difficulty of removal was noted and the remaining HMX/DNPA mixture was cured by conventional procedures. The effect of the process and the additive on the cured composition was then roughly assessed. The liquids

TABLE 4. Castings Prepared by the Prepacked Bed Method of Loading 0.5-inch D by 3-inch Long Cylindrical Molds

HMX size distribution, wt % 20µ/100µ/200µ/Cl.D	Method of packing bed	Binder used	Penetration rate	Cured appearance	% binder		Density range, g/cm³
					Nom	Anal	
25/75/0/0	None	EPX 147-2 + styrene[a]	Fast	Strong, solid[b]	19.4	18.7–19.8	1.650–1.658
25/10/0/65	Vibration	EPX 147-2 + styrene[a]	Very slow	Weak, tacky[c]	12.0	7.5–8.0[d]	1.735–1.744
25/10/0/65	Vibration	EPX 147-2 + styrene[a]	Very slow	Weak, tacky[e]	10.6	8.6–11.5[d]	1.708–1.721
25/10/0/65	Vibration + aspiration	EPX 147-2 + styrene[a]	Very slow	Tacky, porous[c] channeling	Not calc	8.7–9.2	1.736–1.766
25/10/0/65	Vibration + aspiration	EPX 147-2 + styrene[a]	Very slow	Tacky, porous[c]	Not calc	8.1–12.7	1.704–1.721
25/75/0/0	Vibration + aspiration	DNPA	Very slow	Solid, strong[c,f]	19.5	19.3–20.1	---
33/33/33/0	Vibration + aspiration	Aroclor 1221[g]	Moderately slow	---	---	---	---
15/85/0/0	Vibration + aspiration	Aroclor 1221	Fast	---	---	---	---
25/0/75/0	Vibration + aspiration	DNPA	Fast	Solid, strong[c]	10.1	12.6–13.9	---
25/0/75/0	Vibration + aspiration	Aroclor 1221	Fast	---	---	---	---

[a] Styrene added to approximate viscosity of DNPA binder.
[b] Cured without pressurizing.
[c] Pressurized after loading.
[d] Low analysis plus tacky consistency due to styrene volatilization during lengthy bed penetration step.
[e] Temporary pressure after loading.
[f] Less volatile binder. No appreciable loss during loading.
[g] Non-hardening simulant similar in viscosity and surface tension to DNPA.

which appeared the most promising were then further tested in 150 gram batches with production-type mixing and casting apparatus.   Procedures are summarized in Appendix C and preliminary observations in Table 5.

Two liquids, dichloromethane and low boiling petroleum ether (except for its low flash point) were especially promising. Freon 113 also appeared feasible. However, larger scale testing of the latter additive was postponed pending more complete evaluation of the first two. Both of these, on scale-up (Table 6), provided excellent fluidity during mixing, were readily removable, and did not visibly affect curability and physical properties. Resulting castings were solid, dense, and strong. Furthermore, VTS at 150°C and detonation velocity tests failed to reveal any degradatory effects. Additional work is in progress to more fully evaluate the sensitivity of the wet mixes at various stages during processing.

Success with dichloromethane and ligroine points to the advisability of evaluating additional liquids which might offer further improvement. For example, one which was miscible with water would facilitate direct use of HMX which is normally shipped water-wet. Also monomeric liquids might be feasible. These, if incompletely removed, could copolymerize with the DNPA binder thus reducing the possibility of void formation during cure or excessive and non-homogeneous plasticization after cure. Small residual traces of such comonomers should not be sufficient to affect the explosive energy of the final composition.

HMX PARTICLE SIZE DISTRIBUTION. Optimization of HMX particle size to obtain maximum solids loading consistent with processability was described in detail in an earlier report (Ref. 2). Additional work in this field, although comparatively limited, has tended to confirm and substantiate the earlier findings. In recent preparations those particle size distributions found most promising in the initial studies were generally used. Little or no difficulty was experienced in mixing compositions containing up to 87.5% filler when size distribution was optimum and volatile liquids were employed.

As concluded previously, either a 35/10/55 or 25/10/65 20μ-Class A-Class D blend respectively produced the best overall results with DNPA binder and conventional mixing and casting techniques. Raising the percentage of coarse material resulted in greater fluidity with, however, graininess and inferior flow characteristics. Increasing the ratio of fines made the composition softer and more readily extrudable but also limited the solids loading by reducing fluidity. Recent formulations containing optimum distributions combined with DNPA-based binders have been described in Table 6. As predicted earlier, solids loadings of 87% are processable when the distribution is carefully controlled.

TABLE 5. Liquids to Desensitize HMX/DNPA During Initial Stages of Mixing

Additive	Boiling Point, °C	Flash Point, °C	Behavior in Processing, Effect on Cured Composition	Conclusions
Water	100	none	Difficult to remove, emulsifies. Retards cure if traces remain.	Unacceptable.
Methanol	65	18	Difficult to remove. Causes spattering. Resulting specimen very flexible.	Not recommended.
Ethyl acetate	77	5	Completely miscible with DNPA, very difficult to remove. Satisfactory cure except for slight increase in flexibility and very slight porosity.	Not recommended.
Chloroform	61	none	Satisfactory to mix. Final physical properties poor, cheesy and weak.	Not recommended.
Dichloromethane	40	negligible hazard	Satisfactory mixture, readily removed, excellent cured properties.	Acceptable.
Ethyl ether	35	-40	Poor wetting and dispersion, difficult to remove completely, produced weaker and more porous castings.	Not recommended.
Hexane	69	<-23	Formed separate phase. Required prolonged removal. Final casting satisfactory, slightly porous.	Somewhat mediocre.
Petroleum ether	30-45	-12 to -46	Formed separate phase. Readily removed. Excellent final product.	Satisfactory except for flammability.
Freon 113 CCl_2FCCl_2F	46	negligible hazard	Non-homogeneous mix. Hard, dense casting.	Appears satisfactory.

TABLE 6. Properties of 150 Gram HMX/DNPA Batches Prepared With Desensitizing Liquids[a]

Properties	Dichloromethane	Dichloromethane	Petroleum Ether
Composition HMX/binder	87.7/12.3	87.3/12.7	87.4/12.6
HMX Distribution 20μ/Cl.A/Cl.D	25/10/65	35/10/55	28/14/58
Processability	Fluid during mixing, grainy and difficult to cast.	Fluid during mixing, soft with poor flow, slightly difficult to cast.	Fluid during mixing. Soft and fluid at completion, readily cast.
Quality of Castings	Porous due to casting problems.	Excellent, hard, strong.	Excellent, hard, strong.
Cast Density	------	1.807 av. 1.794-1.822	1.808 av. 1.799-1.821
Autoignition Point, °C	------	228	228
Vacuum Thermal Stability, cc/g/48 hrs, 150°C[c]	------	2.8	2.6
Detonation Velocity, m/sec 1/2-in. D.	------	8594	8615
Plate Dent, in.	------	0.11	0.11

[a] 25-30 ml liquid per 130 g HMX. Mixed 1-2 hours at 50°C under vacuum, then cooled before catalyst addition.
[b] 4% ATAC with 0.1% CoAA and 0.5% each tBPB and tBHP.
[c] Re-evacuated after 1 hour, 1-49 hour period.

Bulk density was found to correlate reasonably well with process-ability in highly filled HMX/binder compositions, with the 35/10/55 and 25/10/65 blends yielding the highest values. Several years ago (Ref. 3) attempts were made to predict the processability of 20μ HMX lots used in PBXN-101 preparation by comparing their bulk densities. In this instance correlation was poor.[7] However, in cases where size ranges are more extreme, the relationship apparently becomes more evident and the test may be useful in providing a short-cut for optimization. Examples of the correlation are shown in Table 7. Additional studies along these lines may serve not only to further improve processing and loadability but may also prove of advantage in quality control of HMX blends used to prepare highly filled production compositions.

MODIFICATION OF THE DNPA BINDER

Copolymers With Fluoroalkyl Acrylate

Preliminary small-scale experiments with DNPA and octafluoropentyl acrylate (C_5A) indicated that successful copolymers could be prepared and used as binders for HMX-filled compositions (Ref. 2). A formulation containing 80% HMX with DNPA/C_5A binder, respectively 3:1, cured to a dense, void-free solid with good physical prop rties and good stability.

Since a higher F/C ratio might be advantageous from the standpoint of density and energy, two longer chain fluorocarbon monomers were more recently investigated, and their properties compared with those of the five carbon chain derivative. Initial small scale results are si wn in Table 8.

Although the C_9 monomer was superior in respect to fluorine content[8] and binder density, its poorer processing characteristics tended to nullify these advantages by reducing solids loading. Also physical properties were inferior. Therefore, the C_7 acrylate was selected as the most feasible compromise for scale-up evaluation. Properties of a 150 gram formulation containing this monomer are also described in Table 8. Detonation velocity is essentially the same as that of DNPA homopolymer with comparable HMX loading.

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[7] Twenty micron lots produced varying degrees of fluidity when combined with 100μ HMX and Laminac EPX 147-2 in PBXN-101. Several methods of size determination as well as measurements of bulk density failed to reveal the reason for processing differences. Size as measured by Buckbee-Mears screens was later found to correlate with performance (Ref. 7).

[8] The fluorinated monomers used in these studies were all acrylate esters of α, α, ω-trihydro alcohols. One means of introducing more fluorine into the binder might be to substitute perfluoro derivatives.

TABLE 7. Correlation of HMX Bulk Density With Processability in C. stable DNPA Compositions

HMX Blend, % by Weight				Bulk Density, g/cm³	Processing Characteristics at High Solids Loading With DNPA Binder[a]
20µ	Class A	200µ	Class D		
35	10	0	55	1.380	Best composition for fluidity plus texture. Soft, wet, readily processable.
25	10	0	65	1.358	Wetter than above at same binder level but harder to handle because of graininess.
40	0	0	60	1.344	Gives soft, extrudable texture, requires greater amount of binder to wet. Castable at 14-15% level.
33	33	33	0	1.330	Smooth texture but comparatively dry at 15% level.
50	0	0	50	1.330	Soft, smooth texture but requires >15% binder to wet. adequately.
25	25	0	50	1.330	Poor processability, sandy texture.
15	15	0	70	1.330	Not tried with DNPA binder. Comparatively mediocre with higher viscosity binders.
28	14	0	58	1.330	Good processability, a little grainy but wet and readily castable at <15% binder.
25	0	0	75	1.329	Fluid but excessively grainy, coarse texture.
33	0	0	67	1.301	Gives wet but grainy, coarse mixes. Texture tends to impede flow and extrudability. Castable at 13%.
50	50	0	0	1.266	Not tried with DNPA. With other binders in previous work gave dry mixes at 18% level and higher.
50	0	50	0	1.260	Inadequate data at high solids loadings with DNPA. Expected to be dry.
25	75	0	0	1.250	Smooth texture but dry. Requires 16-17% binder to wet.
75	0	25	0	1.198	No data. Expected to be very dry, as high as 18-20% level.
75	25	0	0	1.162	No data. Same as above.
75	0	0	0	1.130	No data. Same as above.
100	0	0	0	1.026	No data. Same as above.

[a] 7 cstks viscosity.

TABLE 8. Properties of HMX/DNPA-Fluoroalkyl Acrylate Formulations[a]

Fluoroacrylate used	C_5	C_7		C_9
	10 g scale	10 g scale	150 g scale	10 g scale
% F in Fluoro-monomer	53.2	59.1	---	62.6
Density, unfilled binder, g/cm³	1.43	1.44	---	1.47
% HMX filler	80	80	84.6	80
Processability	Best, fluid and castable	Good, sl inferior to C_5	Excellent readily cast	Worst, limited loadability, higher viscosity
Curability	Best, no tack	Similar to C_5, sl tackier	Cured readily	Poorest of group, more tendency for tack and softness
Cured properties	Tough, dense, strong	Slightly softer and more elastomeric	Strong, solid, void-free	Most flexible of three, solid, strong, slightly sticky
Density, g/cm³	1.73	1.72	1.817	1.70
Impact sensitivity, 50% pt, cm	---	36	31	---
Autoignition point, °C Final exotherm Ignition	215 228	216 228	--- ---	214 217
Detonation velocity, m/sec, 0.5 in. D	---	---	8479 (av three shots)	---
Plate dent, inches	---	---	0.11	---
Thermoplasticity, 150°C	---	---	None observed	---

[a] 3:1 DNPA/Fluoroacrylate cured with 4% ATAC, 0.2% DMA, and 0.5% each tBPB and tBHP at 60–80°C.

Further studies are planned based on fluorocarbon compositions, in particular, metallized ones, and theoretical computations are presently being conducted in an attempt to optimize compositions. The results of this work will be reported at a later date.

Copolymers With Difluoroaminopropyl Acrylate

Compounds containing the $-NF_2$ group have come into increasing prominence during the past few years in propellant applications (Ref. 8 and 9). Although promising in respect to energetic properties, their main drawback has been extreme sensitivity to impact and friction. One exception is 2,3-bis(difluoramino)propylacrylate (NFPA) which has an impact value approaching that of TNT.

NFPA was developed by Rohm and Haas Company and is presently being synthesized by this organization in production quantities. Some of its properties are listed in Table 9. Its chemical structure as well as its physical characteristics immediately suggest its applicability as a binder in castable explosive formulations, since it is a low viscosity liquid curable to a relatively hard and strong solid, with high density, favorable potential energy, and heat stability similar to that of DNPA. One drawback might be a high polymerization exotherm; however, in highly filled compositions where the filler could act as a heat sink, this problem should be minimized, especially if curing is carried out slowly at low temperatures.

Ruby calculations were performed to predict the potential energy obtainable from formulations based on NFPA and HMX. Figure 6 shows six simplots for a three-component system containing HMX filler and DNPA/NFPA in varying ratios. Detonation velocity, peak pressure, face-on plate push (FOPP) and side-on plate push (SOPP) are plotted as functions of composition. Methods of computation and their theoretical bases have been described by Dierolf in relation to the present project as well as earlier work at NOTS (Ref. 11, 12).

Study of the simplots shows that at the 85% HMX level there is little overall advantage in substituting NFPA for DNPA. Side-on and face-on plate push relative to PBXN-101 show NFPA superior to DNPA by 1-2%; however, other detonation properties are essentially the same for the two binders.

Experimental studies were undertaken to verify the Ruby calculations. For preliminary evaluation one gram binder formulations were prepared containing DNPA/NFPA 1:1, 1:3, 3:1 and 0:1 respectively. These were mixed with curative systems used for DNPA and for safety and convenience, were cast and cured in Teflon "mini-molds" (Fig. 7). All four binder constituent ratios resulted in similar products, clear, solid, amber-colored polymers with slight flexibility.

TABLE 9. Properties of NFPA Monomer

Formula	2,3-bis(difluoramino)propylacrylate $CH_2(NF_2)CH(NF_2)CH_2$ O C O CH = CH_2
Physical appearance	Low viscosity liquid curing to tough solid similar to DNPA
Molecular weight	216
Density, g/cc[a]	1.25, 25°C
Freezing point, °C[a]	-75
Vapor pressure[a]	1 mm, 20°C
Heat of Formation, Kcal/Mole[a]	-109.28
N_D^{20}[a]	1.4070
DTA, peak exotherm, °C	227[a] at 10°C/minute heat rise 218[b] at 2-3°C minute heat rise
Impact sensitivity, 50% pt.	35 Kg-inches, Picatinny method[a] 40-60 cm, monomer, NOTS method[b] 63 cm, polymer, NOTS method
Friction sensitivity, 10 ZIL[d]	1,000 lb[b]
Electrostatic sensitivity, 12.5 joules	10/10 no fires[b]

[a] Reference 9.
[b] Evaluated by NOTS.
[c] Composition B 36 $\pm$ 3 cm, TNT = 70 cm.
[d] ABL sliding friction (Ref. 10).

Two of the binders, the 1/1 and 100% NFPA compositions,were then formulated with HMX, 30/70 respectively to determine compatibility. Sensitivity tests and DTA indicated results similar to those for HMX/DNPA alone. Furthermore, an HMX/NFPA sample of larger dimensions (0.5"D x 3"H) cured in a 60°C oven evidenced no detectable polymerization exotherm when thermocouples were embedded in the casting.
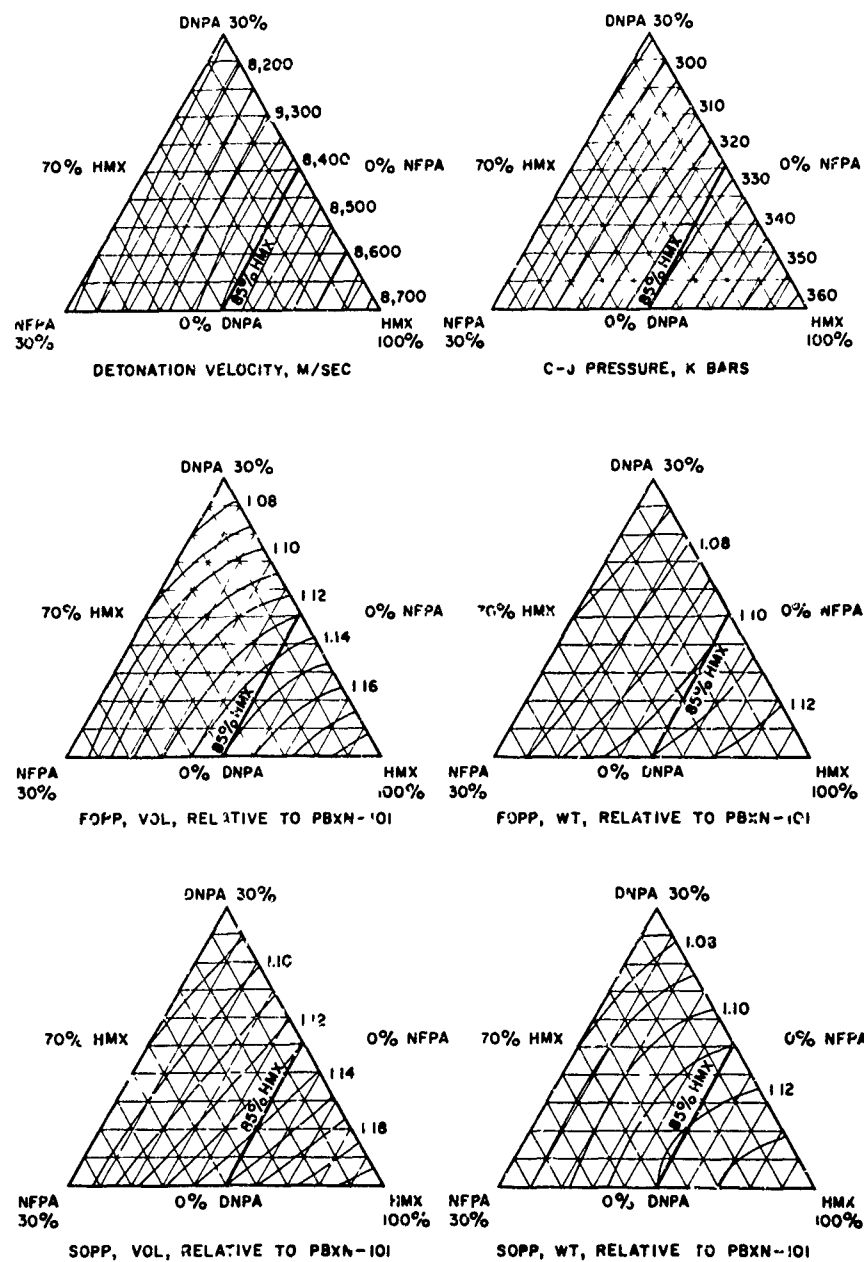
FIG. 6. The Effect of Composition on Explosive Properties. HMX with DNPA and NFPA Binders. Ruby Calculations, 98% TMD.

The 1:1 composition was scaled up to 150 grams to obtain samples for further characterization. The formulation was prepared without incident; processability was excellent, curing was effected without difficulty, and resulting castings were strong, dense, and free from imperfections. Table 10 summarizes the properties of this composition and compares them with those of an analogous formulation containing DNPA as the primary binder constituent. Although experimental results for the detonation velocity of these compositions range slightly higher than computed values, the comparative figures, as predicted, are essentially the same. The composition containing NFPA, however, is inferior in respect to thermal stability.
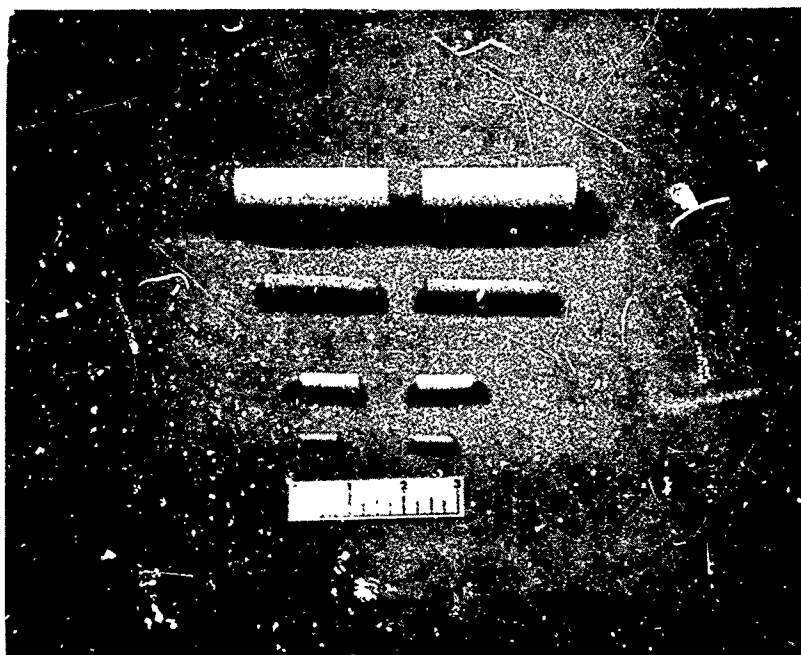

FIG. 7. "Mini-Molds" for Curing Castable Compositions of Questionable Hazard Together With Ejected Castings.

TABLE 10. Properties of HMX/DNPA-NFPA Compared with
Those of HMX/DNPA

Composition	HMX/DNPA-NFPA	HMX/DNPA
Binder comp %	48 DNPA, 48 NFPA, 4 ATAC	95 DNPA, 5 ATAC
Curing agents	0.1% CoAA, 0.5% ea tBPB-tBHP	0.2% DMA, 0.5% ea tBPB-tBHP
Curing conditions	60°C overnight	60°C overnight +80°C 24 hr
HMX content, %	85.2	85.2
HMX distribution, %	35-20μ, 10-class A, 55-Cl D	29-20μ, 14-class A, 57-Cl D
Processability	Excellent, readily castable	Wet but difficult to cast
Appearance of castings	Solid, tough, sl resilient	Slightly porous due to poor castability
Density, g/cm^3	1.799 - 1.817	1.798 - 1.807
DTA exotherms, °C Peak	143, 224 267	204, 256 270
Autoignition exotherms, °C Ignition point	167-175, 185-187, 209 227	218 226
VTS, 150°C	5.3 cc/g/24 hr	3.4 cc/g/48 hr[a] 2.2 cc/g/24 hr
Thermoplasticity, 150°C	Approx 5% deformation ambient to 150°C to ambient in 5 hr	None observable
Det vel m/sec 0.5 in. D	8512	8517
Plate dent, in. 0.5 in. D	0.11	0.11
Impact sens 50%, pt cm	32[b]	28
Friction sens	10/10 no fires, 1300 lb[b]	1/10 fires at 440 lb
Electrostatic sens	10/10 no fires, 12.5 joules[b]	10/10 no fires, 12.5 joules

[a]May be slightly high, CoAA not used.

[b]This was measured on a separate sample, same binder but 80% HMX.

Other Binder Additives

ALLYL TRIFLUOROACETATE. This monomer contains less fluorine (37%) than the trihydrofluoroalkyl acrylates previously described. However, at present it is less costly and more readily available; thus it was examined for possible inclusion in DNPA systems. Four binder compositions were prepared with DNPA, 1:1, 3:1, 1:3, and all fluoromonomer. Failure to cure resulted in all cases, even with 80°C temperature. 2-3 day exposures, and CoAA present. Vinyl trifluoroacetate, like the allyl derivative, failed to cure and also showed definite evidence of incompatibility.

FEFO. 2,2-bis(dinitrofluoroethyl)formal (FEFO), a non-reactive plasticizer, was evaluated with DNPA and NFPA monomers because of its possible favorable contributions to energy, density, and low temperature physical properties (Ref. 13). However, like the vinyl and allyl tri-fluoroacetates, it inhibited curing. Even under fairly stringent conditions of time, temperature and atmosphere, mixtures of FEFO with DNPA, NFPA, or EPX 147-2 failed to cure to desirable consistency.

BDNPF/BDNPA, like FEFO, inhibited curing, and resulting physical properties were unacceptable. Compositions with both DNPA and EPX 147-2 failed to polymerize adequately.

Cross-Linking Agents

Poly-DNPA, when heated to 60-80°C, becomes soft and semifluid. It is therefore necessary in formulating compositions for high temperature use to add a cross-linking agent to prevent plastic deformation. Initial studies (Ref. 2) showed that acetyl triallylcitrate in concentrations of 3-5% was effective in maintaining dimensional stability under load up to 150°C. Diallyl diglycolate, glycol bis-allyl carbonate, ethylene dimeth-acrylate, triethylene glycol dimethacrylate, and triallyl cyanurate were also examined and found inferior to ATAC.

Difficulty and expense in procuring ATAC led to investigation of additional possible substitutes. The results of these studies are summarized in Table 11.

Promising additives were evaluated at both 2 and 5% concentrations in order to estimate minimum required levels. Autoignition tests and vacuum thermal stability measurements were carried out to verify compati-bility. Resistance to thermoplastic deformation was determined by the 100 gram weighted piston test described in a previous report (Ref. 2).

Tetramethylene diacrylate appeared to be even more effective than ATAC, with hard and stable compositions obtained at both 2 and 5% concentration levels. Diallyl maleate was inferior to both ATAC and the diacrylate in that higher concentrations were required to be effective, a disadvantage energywise. Triallyl cyanurate, on reevaluation, showed

TABLE 11. Substitute Crosslinkers for ATAC in HMX/DNPA Formulations, 80/20 HMX-DNPA Cured with CoAA, tBPB and tBHP at 60°C

Additive	% in binder	Appearance after curing	Thermoplasticity 150°C, 100 g wt[a]	Autogn pt, °C[b]	150°C VTS ml/g/48 hr	Remarks
Acetyl triallyl citrate	5	Strong, solid, resilient	No deformation	225	2.4 - 4.2	2% is min effective level
	2	Strong, solid, resilient	Slight deformation, ~80°C	---	---	
Tetramethylene di acrylate	5	Hard, slightly greyish	No deformation	230	2.5 - 2.6	More efective than ATAC at low concentration
	2	Similar to 5%	No deformation	---	---	
Diallyl maleate	5	Hard, dense, strong	Very slight deformation, of questionable significance	229	3.2 - 3.3	Inferior to first two
	2	Similar to 5%	Approx 6% deformation, ambient to 140°C	---	---	
Triallyl cyanurate	5	Hard, slightly flexible	No deformation but considerable darkening in color at 150°C	227	3.9 - 4.8	Questionable compatibility at 150°C
Tetramethylene di methacrylate	5	Incomplete cure at 60°C Crumbly and weak at 80°C	---	---	---	Inhibits cure
Triallylorthoformate	5	Failed to cure at 60 or 80°C	---	---	---	Inhibits cure
Divinyl benzene	5	Failed to cure at 60 or 80°C	---	---	---	Inhibits cure
Tricrotyl orthoformate	5	Failed to cure at 60 or 80°C	---	---	---	Inhibits cure
Diallyl ether	5	Solid, strong	Appreciable deformation starting at 127°C	230	---	Inferior dimensional stability

[a]Described in Ref. 2. Time to 150°C, 20 - 30 min. Sample cooled under pressure 2–3 hours from 150°C to approximately 40°C.

[b]One gram samples, 2°C/min heating rate, HMX ignites at 255°C. Reproducibility ±4°C.

questionable compatibility at 150°C test temperatures. Diallyl ether
failed to provide the desired dimensional stability, and the remaining
comonomers, tetramethylene dimethacrylate, triallyl orthoformate, tri-
crotyl orthoformate, and divinyl benzene inhibited cure.

STABILIZERS FOR HMX/DNPA COMPOSITIONS

One of the main requirements for a new high energy explosive is that
it be sufficiently heat stable to withstand aerodynamic friction generated
under supersonic conditions of flight. A temperature of 150°C has been
specified as an arbitrary minimum goal. To predict whether a given
weapon will withstand certain environmental conditions for a given length
of time without undergoing deterioration which might impair efficiency or
expose personnel to hazards, basic data need to be known such as mass
and heat transfer characteristics of the weapon as well as decomposition
constants for the explosive itself. The latter can be determined by
means of differential thermal analysis employing several rates of heating
and then evaluating the resultant thermograms. These techniques have
been used to predict safe exposure conditions for both propellant and
explosive charges of a given composition (Ref. 14, 15).

Preliminary evaluation of HMX/DNPA because of the large number of
samples and variations involved, was limited to relatively short test
procedures such as standard DTA, autoignition, VTS, and TGA. These
methods were useful in that they afforded a rapid and convenient means
of comparison for preliminary screening purposes. However, since result-
ing values are dependent on environmental variables such as sample size
and heating rate, more refined techniques will eventually be necessary
in order to predict safe conditions for a given charge in a given weapon.
When selection of a definite composition and application warrants, more
complete evaluation may be undertaken.

Preliminary small-scale testing of the HMX/DNPA system has indicated
that stability at 150°C is good provided exposure times are not too
excessive. For example, samples used in thermoplasticity tests showed
only slight darkening in color after exposure.[9] DTA and autoignition
data indicated decomposition exotherms started at about 180°C but were
then interrupted by the HMX endothermic crystalline transition so that
final ignition did not occur until the reference temperature reached 220-
225°C. Gas evolution and weight loss at 150°C were affected to a large
extent by the degree of DNPA polymerization. Respective values averaged
5-7 cc/gram and 3 to 6% over a 48 hour period in initial tests. When
CoAA was used to facilitate cure, these values were reduced by nearly 50%.

In attempts to further improve the heat resistance of DNPA compo-
sitions, a number of different stabilizing agents were added to the
binder at concentrations of 2 and 5%. These included: 2-nitrodiphenyl-

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[9] 4-5 gram cylinder,approx. 30 min to reach 150°C, then cooled to
ambient over 2-3 hour period.

amine, ethyl centralite, Estynox 308, Plastolein 9232, graphite, sodium fluoride, sodium chloride, trisodium phosphate, calcium fluoride, magnesium oxide, 4-dimethylamino-3,5-dinitroaniline, and a 50/50 mixture of Estynox-Plastolein. Some of these materials have been found effective in stabilizing propellant formulations containing either nitro or difluoroamino polymers (Ref. 16).

Detailed results of DTA, TGA, and VTS tests performed on compositions formulated with the various additives are presented in Table 12. Since this work was conducted over a relatively long period of time, extra controls containing no additive were included to afford a better comparison. The main conclusion that can be drawn from studying the results is that none of the additives were effective in improving stability. A few, namely: graphite, sodium chloride, possibly sodium and calcium fluorides, and magnesium oxide appeared to be compatible. The remainder either inhibited cure, accelerated gassing and weight loss, or produced DTA and autoignition exotherms at relatively low temperatures. The most significant stabilizing factor found thus far is, as was shown earlier, the curing agent CoAA.

COATING HMX WITH POLY DNPA

Preliminary studies were carried out to determine the feasibility of coating HMX with DNPA polymer. The objective was two-fold: First, to provide a possible means of desensitizing HMX prior to incorporation in castable mixes with DNPA monomer and, secondly, to prepare a composition suitable for processing as a high-energy extrudable explosive. Since poly-DNPA is soluble in the monomer, its use as a precoating agent should offer some interesting possibilities for formulation without as great a sacrifice in energetic potential as that introduced by comparable inert additives.

Initial work was confined mainly to preparative techniques and hazard evaluation of 85/15 HMX-DNPA mixtures for extrusion. Poly-DNPA dissolved in either ethyl acetate or acetone could be precipitated to coat HMX by addition of either water or aliphatic hydrocarbons. The two major difficulties were obtaining homogeneous coating and desirable agglomerate particle size. The most promising procedure involved precipitation of DNPA dissolved in ethyl acetate onto HMX in an aqueous suspension. Descriptions of some typical products are summarized in Table 13. Sensitivity tests indicate that poly-DNPA applied as a pre-coat does afford some desensitization at the 15% level; however, its efficiency at lower concentrations has not yet been established. Additional sensitivity studies, extrusion results, and use of DNPA coated HMX in castable formulations will be described in a future report.

TABLE 12. The Effect of Additives on the Heat Stability of HMX/DNPA Compositions 75-80% HMX, 5% ATAC in Binder, Cured with tBPB/tBHP and CoAA Where Indicated

Additive	% in binder	Effect on cure	DTA[a] °C Exotherm Onset	DTA[a] °C Exotherm Peak	VTS, 150°C[b], ml/g First hr	VTS, 150°C[b], ml/g Next 48 hr	VTS, 150°C[b], ml/g Wt loss %	TGA 150°C[c] Av wt loss per hr
None[d]	---	---	204	256	0.9	5.7-7.3	2.7-3.3	0.34
None[e]	---	---	204	258	0.7	4.5-5.5	3.3-5.7	0.26
None,[f]	---	---	210g	225g	0.6	3.4-4.8	---	---
2-NDPA	5	None observable	184	187h	1.2	6.7	3.3	0.40
	2	None observable	175-218	258	1.0	7.4	3.0	1.4
Ethyl Centralite	5	Sl retardation	205-213	258	1.0	7.4	3.7	0.94
	2	Sl retardation	204	257	1.1	>10	6.7/29 hr	0.66
Estynox	5	Sl retardation	202	252	1.2	7.1	3.3/43.5 hr	0.93
	2	Sl retardation	196	254	1.0	7.4	4.3	0.91
Plastolein	5	Sl to negligible	194	260	0.9	5.2	4.0	0.76
	2	Sl to negligible	130	133h	0.8	6.9	4.0	0.80
Graphite	5	None observable	205	256	0.7	5.7	3.0	0.79
	2	None observable	205	257	0.8	6.7	3.3	0.63
Na_3PO_4	5	Retarded	190	257	0.9	Off scale	4.7/25 hr	1.3
	2	Incomplete very soft	190-204	267	---	---	---	2.2
NaF	5	None observable	210	256	0.8	8.2	3.3/24 hr	0.98
	2	None observable	208	242	0.6	5.8	6.7/29.5 hr	1.3
NaCl	5	None observable	204	253	0.6	5.2	3.3	0.80
	2	None observable	212	252	0.7	4.6	3.3	0.80
Plastolein/Estynox	5	Some retardation	213	257	0.7	7.1	3.3/42 hr	0.70
	2	Some retardation	205	256	0.8	8.7	5.3/29.5 hr	0.85
CaF_2[f]	5	None observable	---	---	0.6	3.1-4.3	---	---
	2	Very sl retardation	---	---	0.6	5.5	---	---
MgO	5	None observable	---	---	1.1	4.4-5.0	---	---
	2	Sl retardation	---	---	0.9	3.6-4.6	---	---
Dimethylamino di nitroaniline[f]	5	Complete inhibition	---	---	---	---	---	---
	2	Complete inhibition	---	---	---	---	---	---

[a] 3°C/min, 14-53 mg samples.
[b] 2.5-3.0g samples, reevacuated after first hour. Weight loss includes liquid as well as gaseous products.
[c] 70-98 mg samples, 3-7 hr exposure in air.
[d] Aerojet DNPA, NaoH washed.
[e] Aerojet DNPA, distilled. Others contain no accelerator.
[f] CoAA added, 0.1% of binder.
[g] Autoignition test.
[h] This was not final exotherm.

TABLE 13. Properties of HMX[a]/poly-DNPA Slurry-Coated
Compositions

Observations	p-DNPA in Ethyl Acetate HMX in Water	p-DNPA in Acetone HMX in Petroleum ether
Precipitation Characteristics	Discrete granules becoming one soft tacky mass after approx. 85/15 level HMX-DNPA	Immediate coagulation to form one soft tacky mass
Properties of dried product	Forms hard mass unless broken up mechanically prior to drying	Forms hard, tough mass unless broken up prior to drying
Analyzed % DNPA	14.49	15.66
Spread (4 samples)	0.14	0.75
Impact Sensitivity, 50% pt cm	31	29
Friction Sensitivity 10 ZIL[b]	1300 lb	1300 lb
Electrostatic Sensitivity, 12.5 joules[c]	10/10 no fires	10/10 no fires

[a] 1:1:1 20μ/100μ/Class D.
[b] ABL method (Ref. 10). RDX = 300 lb.
[c] Maximum limit of test instrument.

NOTE: See Appendix D for formulation procedure. Test methods are
described in Appendix E.

SUMMARY AND CONCLUSIONS

Significant advances in the development of HMX/DNPA compositions were: higher energy obtained by better processing techniques and simplification of curing resulting from use of CoAA and monomers with low inhibitor content. Modifications in mixing methods not only resulted in greater safety by insuring more complete wetting of HMX but also permitted handling mixes containing nearly 88% explosive filler. Cobalt acetyl acetonate proved to be a valuable additive in promoting more effective cures. Curing times, temperatures and conditions were greatly reduced and simplified. Furthermore, tolerance for impurities such as residual inhibitor was improved and monomer which was inhibited sufficiently to withstand three months at 50°C could be adequately cured without prior washing or distillation. CoAA-cured compositions not only were stronger and harder, they also evidence greater heat stability presumably through reduction in loss of free monomer.

Two new binders were formulated based on combination of DNPA with C_7 fluoroalkyl acrylate and difluoramino propylacrylate. Resulting polymers were clear, solid, strong, and slightly flexible. When formulated with 85% HMX, these binders showed approximately the same explosive potential as that of DNPA homopolymer. This experimental observation verified theoretical computations which predicted negligible changes in energy resulting from inclusion of NFPA.

DNPA monomer obtained over a period of several years from various sources was found to be consistent and curable in all cases to excellent end products of comparable strength and stability. Accelerated surveillance tests to determine minimum inhibitor levels as well as experience with routine storage of purified monomer over a period of several years indicated that excellent shelf life may be anticipated without excessive amounts of inhibitor requiring removal by laborious methods prior to final processing.

RECOMMENDATIONS FOR FUTURE WORK

Planned work falls into two general categories: Further improvement of the present HMX/DNPA composition, and investigation of new but related systems.

In the first area, additional methods are being sought to evaluate explosive effectiveness (Ref. 17). This approach should prove of interest not only in better characterizing the DNPA formulation but also in further correlating theory with actual performance.

Attempts should be continued to increase solids loading without sacrificing processability. Previous experience indicates that use of desensitizing liquids in mixing combined with optimizing HMX size and shape may permit up to 88-89% filling which is probably maximum for this approach. Increases of several percent, however, may be possible by

36   CONFIDENTIAL

perfecting the "prepacked bed" method. Thus, loadings of over 90% plus the possible contribution of new additives and modifications in binder may well result in raising detonation velocities to 8700 meters per second or even slightly higher.

Poly-DNPA may be used to good advantage as a binder for extrudable explosives and possibly propellants as well. Although this application is somewhat outside of the scope of the present project, the properties observed for DNPA suggest its applicability. Its thermoplasticity would permit processing at low temperatures. Its inherent energy would provide considerably better explosive potential than afforded by inert binders now in use. Furthermore, experiments have shown that it can be successfully coated on HMX in both aqueous and non-aqueous slurries to produce a molding powder with sensitivity similar to that of tetryl.

Calculations are presently being performed to predict the effect of metals such as aluminum in systems containing HMX or RDX with DNPA, NFPA, and C_7A. Solids loading in these cases should be excellent due to the shape and surface characteristics of the metal additive. Initial studies thus far indicate no compatibility or processing problems.

Further studies should be carried out to better characterize the stability of HMX/DNPA formulations compounded under the most favorable conditions known at present. Such factors would include optimization of both curing environment and composition, including choice of curative, crosslinker, and stabilizer. Sufficient basic data should be obtained regarding decomposition rates and physical constants so that stability may be calculated over a wide range of environmental conditions.

In the area of new binders, attempts are being made to optimize a high-energy structure by minimizing CH_2 groups and raising the percentage of NO_2 and F. This involves the synthesis of new unsaturated esters to replace DNPA, serve as copolymers for DNPA, or precoat HMX. Examples might be dinitropropyl maleate or fluorodinitroethyl acrylate. New NF_2 derivatives might also be included in this study, sensitivity and stability permitting. Also solid oxidants and dense additives will continue to be investigated. Thus, by a combination of approaches—higher solids loading, more energetic binders, and better stabilization—it is anticipated that still further improvement of the existing HMX/DNPA system may result, leading to both a superior explosive and better understanding of explosive phenomena.

Appendix A

MATERIAL USED

Common solvents and chemicals were either reagent grade or the purest grade commercially availab

Chemical	Supplier	Lot no.	Date rec'd	Remarks
Acetyl triallyl citrate	Miles Chemical	14	12-66	BP 142-143°C/0.2mm
	K & K Laboratories	6397	---	---
Allyl trifluoroacetate	Peninsular Chemresearch	3156-A1-40	8-66	---
Aroclor 1221	Monsanto	B-8	1-64	---
BDNPF/BDNPA	Aerojet	90-6	6-4-66	---
bis-(2,2-dinitro-2-fluoroethyl) formal (FEFO)	NOL/WO	?84?, 730	---	---
bis-2,3-(difluoroamino)propyl acrylate	Rohm & Haas Co	---	---	---
Calcium fluoride	Matheson/Coleman	---	---	Reagent grade
C5 Fluoroalkyl acrylate	duPont	---	---	1,1,5 trihydro, redistilled
C7 Fluoroalkyl acrylate	duPont	---	---	1,1,7 trihydro, redistilled
C9 Fluorcalkyl acrylate	duPont	---	---	1,1,9 trihydro, redistilled
Cobaltous acetyl acetonate	Shepherd Chemical	039-902	7-66	---
Cobalt octoate	Nuodex	3988	1-65	---
Cobalt propionate	Shepherd Chemical	033-032-5194	7-66	---
Diallyl ether	Borden 7344	500-6-6	10-65	---
Diallyl maleate	Eastman P5364	MP12-1-60	3-61	---
Divinyl benzene^a	Borden	82048	---	Purified
Dimethyl aniline	Baker	---	---	---
4-dimethylamino-3,5-dinitroaniline	Aldrich D-14070	---	---	inhibited with methylene blue
2,2-dinitropropyl acrylate (DNPA)	Aerojet	AGC 4651-2/A.H. Swift	7-62	0.02% HQ
2,2-dinitropropyl acrylate (DNPA)	Aerojet	AGC 06824/J.S. Scigliano	12-65	0.02% HQ
2,2-dinitropropyl acrylate (DNPA)	Aerojet	---	1-67	0.1% MEHQ
2,2-dinitropropyl acrylate (DNPA)	Hummel	NL 12-36	4-66	No added inhibitor
2,2-dinitropropyl acrylate (DNPA)	Hummel	NL 12-73-6-228	8-66	50 ppm MEHQ
2,2-dinitropropyl acrylate (DNPA)	Northrup/Carolina	8996-42	8-66	---
Ethyl centralite	duPont	85027	---	---
Estynox 308	Baker Castor Oil	171-58 BF27	---	Epoxy acetoxy stearin
HMX	Holston Ordnance Works	2-63, BC263B	---	Twenty micron^b
HMX	Holston Ordnance Works	1-63	---	Class A^b
HMX	Holston Ordnance Works	3-61	---	Class D^b
HMX	Holston Ordnance Works	---	---	200 micron^b
Hydroquinone	Braun Chemical	---	---	Photo grade
Laminac EPX 147-2	American Cyanamid	A-152-60	2-60	Reagent grade
Magnesium oxide	Baker 2476	---	---	---
2-nitro diphenylamine	Eastman 3906	---	---	---
Plastolein 9232	Emery	---	---	---
Sodium fluoride	Baker	---	---	---
Sodium phosphate	Braun Chemical	---	---	---
Styrene	Eastman 1465	---	---	Reagent
t-butyl hydroperoxide	Ram Chemical	T.D. 152	8-61	---
t-butyl perbenzoate	Ram Chemical	132-108	1963	---
Tetramethylene diacrylate	Borden	MP 10-11-60	10-65	---
Tetramethylene dimethacrylate	Borden	MP W60305	3-61	---
Triallyl cyanurate	Borden	---	3-61	---
Triallyl orthoformate	Kay-Fries	---	1-66	---
Tricrotyl orthoformate	Kay-Fries	---	1-66	---
Vinyl crotonate	Millmaster	BS 4122	---	BP 131-134°C
Vinyl trifluoroacetate	Peninsular Chemresearch	3156 A1340	---	---

^a 55.1% divinyl benzene, 37.7% ethyl vinyl benzene, 2.1% diethyl benzene.
^b Complete particle size data may be found in Ref. 2.

APPENDIX B

PURIFICATION PROCEDURES FOR DNPA MONOMER

1.   Caustic Wash

     100 ml of DNPA was placed in a 250 or 500 ml separatory funnel.
     10 ml of the following solution was added and the mixture shaken
well:

          100 ml H_2O
          20 g NaCl
          5 g NaOH

     The top layer was discarded and the extraction repeated up to
three times.

     The DNPA was then treated with six 50-ml distilled water washes,
dried over anhydrous $MgSO_4$ for two days, then filtered and stored under
refrigeration.

2.   MgO Extraction

     100 ml DNPA and) g MgO were agitated for three hours.
     The MgO was then filtered off and the DNPA stored under refrigeration.

3.   Caustic Wash Plus MgO

     DNPA washed twice with caustic solution and six times with water
followed by $MgSO_4$ drying was stirred with MgO for 2-3 hours. The MgO
was then filtered off.

4.   Distillation

     DNPA monomer was vacuum distilled twice at 1-2 mm pressure with
steam as heat source. Boiling point: 62-78°C.

APPENDIX C

PREPARATION OF COMPOSITIONS

Preliminary laboratory-scale formulations were hand-mixed in either one or ten-gram batches by combining premixed binder with HMX required to make a 20/80 composition respectively. The product was then loaded into Teflon molds, vibrated, and cured either in closed nitrogen-filled vessels or directly in ovens.

Larger batches up to 150-200 grams were prepared remotely in a Baker-Perkins model 2-PX one-pint mixer as described in Ref. 2. Slow mixing speeds were employed until the HMX was wetted by the binder and/or the desensitizing liquid if the latter was included in the formulation.

To remove volatile desensitizers 50°C heat and vacuum were applied with additional evacuation during final stages of mixing and casting. The composition was cured in 0.5-in. by 3.0-in. cylinderical Teflon molds with vibration during casting to facilitate compaction.

APPENDIX D

SLURRY PROCEDURES FOR PRECOATING HMX WITH POLY-DNPA

Variations of the following basic procedure were used to prepare HMX coated with 5 and 15% poly-DNPA.

The DNPA was dissolved in solvent, either ethyl acetate or acetone or a combination.

HMX and water were introduced into a three-necked flask fitted with dropping funnel, "Tru-Bore" stirrer, and vacuum inlet.

The DNPA was added dropwise to the agitated HMX suspension.

A steam bath was then placed under the assembly and heat and vacuum were applied to remove most of the organic solvent.

The resulting coagulant was filtered off and dried in an air stream at ambient or slightly elevated temperatures.

APPENDIX E

TEST PROCEDURES

Autoignition

One gram samples heated in metal block at rate of 2°C per minute. Ignition temperature recorded as temperature of block when differential thermocouple to sample indicates final exotherm.

Vacuum Thermal Stability

2.5 to 3.0 gram samples. Gas volume emitted during first hour was recorded and sample was then reevacuated. Zero time for given data starts after reevacuation. Details are in Ref. 18.

Differential Thermal Analysis

14-53 mg samples heated at 2 to 3.5°C per minute.

Impact Sensitivity

35 mg samples, 2.5 Kg weight, with sandpaper and equipment described in Ref. 18. Samples are pelletized where feasible. Composition B 50% point by this method is 36 ± 3 cm and HMX is 18-22 cm.

Friction Sensitivity

The ABL method for sliding friction was used. By this method 10 ZIL (10/10 no fires, zero initiation level) for RDX is 300 lb, for 75/25 Octol 700 lb, for tetryl 700 lb, and for Composition B - 1000 lb. Details are described in Ref. 10.

Thermoplasticity

A cylindrical specimen 1/2-in. in diameter by 2-3-in. high is placed in a graduated cylinder with a 100 gram weighted piston resting on the sample (Ref. 2). The assembly is immersed in an oil bath behind a shield and the temperature is raised to 150°C within a 20-30 minute period. The temperature at which any deformation occurs is noted. The sample is then cooled to ambient and any further deformation noted.

Electrostatic Sensitivity

50 mg samples, 1 µFd capacitor, variable voltage to 5000 maximum, (12.5 joules) 25 shots per test.

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13. ABSTRACT

ABSTRACT. The castable explosive, HMX/dinitropropylacrylate, was improved by formulation modifications to obtain higher energy, better physical properties and stability, and greater efficiency in preparation. Use of volatile liquids in mixing operations, special casting techniques, and selection of optimum HMX particle size blends resulted in solids loadings of 87% and higher with corresponding detonation velocities exceeding 8600 meters per second. Optimization of monomer inhibitor concentration made it possible to eliminate pre-processing DNPA purification, yet at the same time obtain adequate storage stability. Use of a new curative, cobalt acetyl acetonate, greatly facilitated curing by reducing time and temperature and eliminating the necessity for oxygen exclusion. Resulting castings were harder, more uniform, and more stable, with 150°C VTS values as low as 2.4 cc/g/48 hours. (C)

Two new copolymers of DNPA were prepared and evaluated as energetic binders, one with difluoraminopropylacrylate, the other with dodecafluoroheptylacrylate. Detonation velocities, as predicted by computation, were comparable to those for DNPA homopolymer at equivalent HMX loadings. (C)

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14.			LINK A		LINK B		LINK C	
KEY WORDS			ROLE	WT	ROLE	WT	ROLE	WT
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HMX								
Dinitropropylacrylate								
PBX (Cast)								
Detonation Velocity								
Physical properties								
Polymer								
Copolymer								

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China Lake, Calif., NOTS, June 1967. 46 pp. (NOTS TP
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ABSTRACT. A castable explosive HMX/dinitropropyl-
acrylate, was improved by formulation modifications
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casting techniques, and selection of optimum HMX particle size blends resulted in solids loading of 87% and higher with corresponding detonation velocities exceeding 8600 meters per second. Optimization of monomer inhibitor concentration made it possible to eliminate pre-processing DNPA purification, yet at the same time obtain adequate storage stability. Use of a new curative, cobalt acetyl acetonate, greatly facilitated curing by reducing time and temperature and eliminating the necessity for oxygen exclusion. Resulting castings were harder, more uniform, and more stable with 150°C VTS values

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computation, were comparable to those for DNPA homo-
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